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Report of the FAO/UNEP/WHO/IOC/IAEA

MEETING ON THE BIOGEOCHEMICAL CYCLE OF MERCURY IN THE MEDITERRANEAN

Siena, Italy, 27-31 August 1984

prepared as part of the

Long-term Programme for Pollution Monitoring and Research in the Mediterranean (MED POL Phase II)

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

Report of the

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Rome, 1985

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PREPARATION OF THIS REPORT

This report was prepared as part of a cooperative project of the United Nations Environment Programme, entitled:

Mediterranean Action Plan: Support to the Implementation of MED POL-Phase II

with the Food and Agriculture Organization of the United Nations,
the United Nations Educational, Scientific and Cultural Organization,
the Intergovernmental Oceanographic Commission,
the World Health Organization,
the World Meteorological Organization, and
the International Atomic Energy Agency,
as cooperating agencies.

The papers presented at the meeting will be published as a supplement to this report.

DEFINITION OF MARINE POLLUTION

Pollution of the marine environment means: "The introduction by man, directly or indirectly, of substances or energy into the marine environment (including estuaries) which results in such deleterious effects as harm to living resources, hazards to human health, hindrance to marine activities including fishing, impairment of quality for use of sea water and reduction of amenities".

IMO/FAO/Unesco/WMO/WHO/IAEA/UN/UNEP Joint Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP)

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1. BACKGROUND

It is widely recognized that the Mediterranean area is a region of enhanced mercury occurrence. Tectonically, it is an active region and is rich in mercury deposits. Active mining sites in the Mediterranean account for about 50% of the world's mercury production. The above information, combined with the known toxicity of the metal, has led to increased public concern.

One of the general objectives of the Joint Co-ordinated Mediterranean Pollution Monitoring and Research Programme (MED POL - PHASE I) which was initiated in 1975 and formally approved by the Intergovernmental Meeting on the Protection of the Mediterranean (Barcelona, 28 January - 4 February 1975) as the scientific/technical component of the Mediterranean Action Plan, was to carry out analyses and to build up a consistent time-series of data on the sources, pathways, levels and effects of pollutants in the Mediterranean Sea.

One of the pilot projects of MED POL-PHASE I was concerned with baseline studies and monitoring of heavy metals, particularly mercury and cadmium, in marine organisms (MED II). The data on mercury in the Mediterranean accumulated in the framework of this pilot project, and other relevant data, have been used in an assessment of the state of mercury pollution in the Mediterranean Sea (UNEP/FAO/WHO, 1983).

The MED POL-PHASE II Programme is basically divided into two groups of activities, namely Monitoring and Research. The Research Component is divided into twelve topics one of which is concerned with the biogeochemical cycle of specific pollutants within which mercury receives a high priority (research activity "K").

Within the framework of research activity "K" a meeting was jointly convened by FAO, UNEP, WHO, IOC and IAEA on the biogeochemical cycle of mercury in the Mediterranean. FAO undertook technical responsibility for the meeting.

The meeting took place in Siena, Italy, from 27 - 31 August 1984 at the kind invitation of the Department of Environmental Biology, University of Siena, and was attended by 33 participants (See Annex I). Professor A. Renzoni was elected Chairman, Professor Y. Halim, Vice-Chairman and Dr. D. Zafiropoulos, Rapporteur. Dr. G.P. Gabrielides, FAO Senior Fishery Officer (Marine Pollution), acted as Technical Secretary.

The meeting had the following objectives:

a) to review the progress of the on-going projects undertaken in the framework of research activity "K". Mediterranean Scientists reported on their work by presenting various papers (See Annex II);

b) to define the various biogeochemical processes and pin-point information gaps in the cycle;

c) to produce a report which would contain all available information on the topic;

d) to recommend topics for future research.

The papers presented at the meeting are published in a separate volume. The present report was prepared and adopted by the meeting on Friday, 31 August, 1984.

2. BASIC PROCESSES

The basic processes which control the distribution, behaviour and fate of mercury in the marine environment are controlled by its chemical, physical and biological features and by the dynamic nature of the ocean-atmosphere. In this discussion, the approach is to begin with the chemical properties and reactions of mercury which lead to its contribution to the marine environment from land-based sources. Emphasis is placed upon those features which make mercury different from other trace metals in biogeochemical cycles.

2.1. Natural sources and weathering

Mercury occurs in the Earth's crust in three principal forms, sulphides (dominantly cinnabar, HgS), oxides and native mercury. Sulphide minerals at the Earth's surface are susceptible to oxidation by atmospheric oxygen. Also, mercury oxides and native mercury are subjected to weathering reactions, mainly promoted by hydrogen ion activities in precipitation, surface and ground water. All of these weathering processes lead to the mobilisation of mercuric ions (Hg^{2+}) into surface and ground waters. This represents the start of one of the two main routes of mercury transport to the oceans, the other being atmospheric transport.

One important aspect of air/sea exchange of mercury is the direction of the net flow. At present, analytical difficulties make it impossible to collect enough data on mercury concentrations (especially for sea surface water and the atmosphere immediately above the ocean) to compute the net flow based on solubility and volatility considerations and taking into account likely spatial and temporal variations. The release of volatile mercury species in upwelling ocean areas is further discussed below.

Once in solution, Hg^{2+} ions are readily complexed by inorganic and organic ligands. The nature of these complexes will, of course, vary with the composition of surface waters. Also Hg^{2+} ions show a strong tendency to adsorb onto particulate matter, i.e. soil and sediment particles. Mercuric ions are adsorbed by natural organic matter, particularly through Hg^{2+} reactions with organic sulphur sites in proteinous materials, the negative surface charge sites found on silicate minerals (especially clay minerals) and the ubiquitous Fe/Mn oxy-hydroxide and sulphide phases of soils and sediments.

During the physical transport of mercury in solution and in association with suspended matter in rivers and ground water a number of chemical transformations may be expected. One of these processes is the conversion of inorganic mercury to alkyl forms, especially methyl and dimethyl mercury which are volatile and can be lost to the atmosphere. The chemistry and biochemistry of this important aspect are discussed in more detail below (section 2.3.).

Water-borne mercury from weathering processes reaches the oceans through the estuarine environment where further transformations occur as fresh and saline waters mix together.

Some mercury from natural sources on the continents will reach the oceans directly through the atmosphere. This occurs because of the volatility of native mercury and many of its compounds. In addition to these volatile losses from rocks and soils, mercury also enters the atmosphere from local volcanic and geothermal sources. These atmospheric contributions reach the oceans through dry and wet deposition processes, following the slow oxidation of elemental mercury and the degradation of dimethyl mercury by photochemical processes and/or through atmospheric acidity.

2.2. Anthropogenic sources

Many of man's activities lead to the unintentional mobilization of mercury at the Earth's surface. Examples of such activities are quarrying, mining, agricultural practices, fossil-fuel burning and the incineration of domestic and industrial wastes.

Mercury is used because of its unique properties in various industrial, agricultural and pharmaceutical activities. Important sources in terms of the quantity available for transport to the oceans, either directly through surface waters or via the atmosphere, are from the chlor-alkali industry, where mercury is present in aqueous and gaseous effluents after its use in electrodes for the electrolysis of brine, and from the application of organo-mercurial agrochemicals to control fungi and other pests. Many of these agrochemicals contain phenyl and alcoxyalkyl mercury compounds which are gradually degraded to inorganic mercury.

The sources of these anthropogenic contributions of mercury tend to be localised, and variable in the nature of the mercury-containing materials present. Hence, it is very difficult to generalise about the chemical processes taking place during their

transport to the oceans. However, most chlor-alkali derived mercury will be present as elemental mercury, inorganic Hg^{2+} or mercuric sulphide forms which will undergo the same complexation and particle interactions discussed above. Many of these effluent discharges are directly to coastal waters or estuaries, as well as to river systems.

2.3. Mercury in the marine biogeochemical cycle

Removal to Marine Sediments

Before moving on to discuss the interesting and important conversion of inorganic mercury to alkyl forms, it is worthwhile to outline the fate of mercury which will pass through the marine chemical cycle and finally deposit in marine sediments.

Mercury entering ocean surface waters from riverine or atmospheric sources will be distributed between "dissolved" and "particulate" phases. In chemical oceanography these are essentially operationally defined parameters. Studies have shown that, quantitatively, mercury is mainly in particulate forms, and these finally deposit within marine sediments. The accumulation and burial of these deposits is a process by which mercury, along with many other chemical elements, are removed from the Earth's surface geochemical cycle. The concentrations of mercury in these sediments, in common with all other sediments (eg. rivers, lakes, estuaries), are highly dependent on the lithological and mineralogical properties of the sediments. Strong correlations exist between the mercury content of sediments and the percentage of fine grained materials, i.e. clays and silts. Mercury is enriched in organic phases and sulphides. Thus, carbonate and silica-rich sediments are expected to be depleted in mercury.

Transformation

Methylation of mercury occurs in the terrestrial, limnic and marine environments. The process can be biologically mediated or abiotic. A wide range of micro-organisms have been found able to produce methylated forms of mercury from inorganic species. From the point of view of the microbes, methylation of mercury in a similar fashion to the formation of elementary mercury, is a detoxification process that also provides a route for excretion. Several biochemical pathways have been described for the biological methylation of mercury, e.g. via methylcobalamine and methiomine syntheses. Methyl mercury is then released to water, taken up by organisms and enriched along the food chain as described below.

Intensive production of volatile mercury compounds such as elemental and/or dimethyl mercury in upwelling areas have been reported to result in elevated levels of atmospheric mercury. As biological methylation occurs when microbes incorporate mercury-coated organic particles, methylation takes place both within sediments and on particles suspended in the water column. The ability of methyl mercury to pass through cell membranes, which for the bacteria provides a route for excretion, gives rise to severe problems especially for mammals with highly developed cerebral nervous systems and sensitive foetuses. The protective barriers, e.g. the blood/brain and placenta barriers which protect against toxic compounds, are ineffective against methyl mercury transport. In consequence, fish-eating marine mammals with a high intake of methyl mercury have developed methyl mercury-degrading enzymes. Furthermore, these mammals produce mercury selenide (HgSe) as a detoxified form which they store in high concentrations in the liver.

Bioavailability, uptake and accumulation

The bio-availability of mercury is directly related to its physical and chemical forms in the environment. The inorganic bioavailable forms influence the entry of mercury into organisms at the lowest end of the food chain, mainly through surface adsorption processes. In addition, these forms can be taken up by higher organisms (e.g. molluscs, crustacea, fish) through the gills and/or by food ingestion. Characteristically, such uptake is accompanied by high depuration rates and thus a form of "steady state" situation between the organisms and their environment is approached.

Organic mercury is almost exclusively present as monomethyl mercury in the marine environment. This chemical species is produced from both biotic and abiotic processes (see above), and is characterised by its efficient uptake by organisms with very low elimination rates. This leads to high accumulation, especially in high trophic levels, where the topmost predators can represent a high risk population especially in polluted areas. A consequence of the high bioaffinity of methyl mercury is that it is predominantly associated with living and dead organic materials, and is not in a simple "steady state" relationship within the environment. This feature may become important when the recovery of mercury polluted environment is considered.

When methyl mercury-rich species of marine predators die they will most likely be consumed by other scavengers which will then accumulate the methyl mercury. If the methyl mercury-rich species are decomposed by bacteria, then the results obtained from fresh water systems suggest that the methyl mercury may be either decomposed or converted into dimethyl mercury and released to the atmosphere.

3. SOURCES AND BUDGET CALCULATIONS

Inputs of mercury to the Mediterranean basin have been assessed by the Joint MED POL X Project the results of which are given in the report "Pollutants from land based sources in the Mediterranean" (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA,1984).

The sources considered in the project were the following:

(i) Domestic waste water
(ii) Industrial waste water
(iii) River discharges

The atmospheric fallout was not considered at all. The results of this project should be considered as a first approximation, based on insufficient data, and on results, the reliability of which is in many cases doubtful. Moreover, the different investigators have measured different forms of mercury such as "total" or "dissolved" or "reactive". On the other hand, experience acquired in sea water analysis in recent years shows that most of the data prior to 1975 - 1980 are probably invalid. It is obvious therefore that a renewed effort must be made towards a more rigorous and more complete assessment.

3.1. Rivers

The reservations made about the validity of measurements for sea water are equally true for river water concentrations, and as a consequence, the fluxes given in MED POL X may not be realistic. More recent analyses of dissolved mercury in Italian and other rivers (Breder et al., 1981; Martin, unpublished data) often show concentrations between 5 and 25 ng l^{-1}, including the results for rivers in industrialized zones. The MED POL X estimates for dissolved mercury should probably be reduced by a factor of 5 to 10, and an intensive survey of Mediterranean rivers must be carried out. Simultaneous measurements of the suspended particle load in the rivers must be made, paying attention to:

a) fluctuations during flood periods
b) estuarine processes which can drastically change the flux of dissolved and particulate mercury forms to the Mediterranean.

The flocculation and sorption processes which may occur at the freshwater/sea water interface must be carefully assessed for some representative estuaries.

3.2. Industrial waste water

Direct industrial inputs to the Mediterranean have been estimated at about 6% of the total mercury input (UNEP/ECE/UNIDO/FAO/UNESCO/WHO/IAEA, 1984). Several chlor-alkali plants are located along the coasts of the Mediterranean and only very few have adopted any means of control of mercury release in their wastes. Estimates of

their input are often based on tentative approximations of the total amount of mercury lost to the environment by the industrial plant and replaced every year. For many other chlor-alkali plants even this indirect information remains out of reach of scientists. In all situations, direct measurement of both dissolved and particulate mercury in the outflowing waste water from the effluent has to be made repeatedly and the rate of input of both forms assessed. The apparently relatively small contribution of mercury in industrial wastes compared to other sources in the Mediterranean (as reported by MED POL X) must be reassessed and its potentially drastic effect on the local environment must not be underestimated.

3.3. Domestic waste water

The mercury contribution of domestic waste water to the Mediterranean basin is estimated by MED POL X to be about 0.6% of the total. Domestic waste water in most Mediterranean coastal cities consists of a mixture of sewage water with waste water from numerous small factories released without pretreatment. The mercury content of this type of waste water with heavy loads of organic material is not known with any certainty and requires further investigation.

3.4 Inputs from the atmosphere

Atmospheric input of mercury has not been considered in MED POL X and very few data are available for the world oceans. In a global budget, Lindqvist et al. (1984) estimated the total deposition rate to be between 4 and 30 g km^{-2} $year^{-1}$. For the Mediterranean it can be assumed that this "background" flux is enhanced by the vicinity of the industrial zones, mainly in western Europe, and by volcanic activity. Arnold et al. (1983) estimate a deposition rate of about 50 g km^{-2} $year^{-1}$ from measurements carried out during an oceanographic cruise in the Western Basin. If extrapolated to the total area of the Mediterranean basin, this estimate would give an input rate of about 150 t $year^{-1}$. Such estimates, for the time being, may be regarded as an approximation of the order of magnitude indicating that atmospheric fallout is probably no less important an input than river inputs.

3.5. Outputs

Several outputs of mercury are possible; re-emission of mercury from sea water to the atmosphere, outflowing Mediterranean waters through the straits of Gibraltar, and sedimentation. A small amount of mercury is also removed through fisheries. No reliable data are yet available for these outputs.

3.6. Net balance in the straits

Mass exchanges in the straits are quite well known from water and salt budgets (see for example Bethoux, 1980). Mercury exchanges also occur in the straits of Gibraltar. It is probably too early to have a very reliable balance for these straits but it is evidently important; on the basis of just one ng l^{-1} difference in the mercury concentrations between inflowing Atlantic waters and outflowing Mediterranean waters, and of an inflow of $50X10^{12}$ m^3 $year^{-1}$ (equilibrated by a nearly equivalent outflow), we should find an input (or an output) of 50 t $year^{-1}$ of mercury.

4. LEVELS IN THE MEDITERRANEAN

4.1. Sea water

The accurate determination of mercury concentrations in sea water is extremely difficult in view of the many complications and uncertainties involved. Mercury concentrations are very low and serious errors can arise due to contamination and/or loss of mercury. Contamination of sea water samples can occur during sampling, handling and storage or during pretreatment, filtering or preconcentration steps. Due to such difficulties the concentration values reported for mercury in sea water have decreased

over the past 10 years. Brewer(1975), reviewing mercury concentrations in sea water has reported values around 30 ng l^{-1}. Other authors reported "typical" oceanic concentrations ranging from 10 to 200 ng l^{-1} (Fitzgerald and Lyons, 1973; Windom et al., 1975; Robertson and Carpenter, 1976; Baker, 1977).

In recent years major progress in sampling, pretreatment and analytical instruments, and ultra clean methods has led to more reliable determinations. Bruland (1983) has pointed out that although the oceanic distribution of mercury is still not completely understood, recent measurements suggest that open ocean concentrations appear to lie in the range of 0.5 - 5 ng l^{-1}. Olafsson(1983) has reported no significant differences between mercury concentrations in Atlantic ocean water masses. Fitzgerald et al.(1983) working with Central Pacific surface water reported reactive mercury concentrations of 5 ± 2 ng l^{-1} whereas Nishimura et al.(1983) reported mercury concentrations in North and South Pacific waters in the range of 3-6 ng l^{-1} with a mean of 5.3 ng l^{-1}. Bloom and Crecelius(1983) have reported even lower concentrations ranging from 0.2 to 1 ng l^{-1} in certain coastal waters. It is apparent that accepted "typical" oceanic concentrations have decreased by about two orders of magnitude during recent years. Early studies in the Mediterranean have reported open water values ranging from 14 to 40 ng l^{-1} for dissolved and 110 - 120 ng l^{-1} for total mercury (Robertson et al., 1972; Huyn-Ngoc and Fukai, 1979). Recent publications report concentrations that are considerably lower and range from 0.5 to about 20 ng l^{-1} (Buat-Menard et al.,1981; Aston et al., Copin-Montégut et al., and Salihoglu (present meeting)).

A review of the results of an ICES intercalibration exercise for the determination of "dissolved" mercury in sea water, (Olafsson, 1982), suggests that there are difficulties in accurately analysing open ocean waters. The results reported by 32 laboratories for the analysis of a sea water sample ranged from 1 to 64 ng l^{-1}. In view of this, it is doubtful whether the results of analyses of open-ocean waters from different regions (including the Mediterranean) and analysed by different laboratories are really comparable.

Concentrations of total mercury in coastal waters of the Mediterranean have been reported to range between 12 and 190 ng l^{-1} (UNEP/FAO/WHO,1983). More recent data are in the range of 0.5 -20 ng l^{-1} in unpolluted coastal waters of the Western Mediterranean Basin (Copin-Montégut et al., present meeting). High concentrations occur in coastal waters receiving domestic and industrial wastes, chlor-alkali plant effluents, and run-off from areas where mining activities occur. It should be pointed out that a considerable variability of mercury concentrations in coastal waters should be expected as a result of factors such as input levels variation, currents, upwelling etc. It should also be noted that total concentrations of mercury in Mediterranean sea water are of rather limited value if the different physicochemical forms are not known (see section 2.3.3.). Previous studies suggest that dissolved mercury is the major form in open ocean waters. On the contrary, in coastal waters particulate mercury has been reported to be around 75% of total concentrations (El Rayis et al., present meeting). Clearly, in attempting to evaluate the uptake of mercury by marine organisms, information on the organic versus inorganic forms of dissolved mercury is also necessary (see section 2.3.).

4.2. Sediments

Due to the relatively higher concentrations of mercury in marine sediments, analytical determinations are reasonably reliable. However, mercury concentrations will depend on factors such as the organic content, sediment grain size distributions and mineralogical characteristics, especially carbonates. An additional factor that has to be taken into account in evaluating sediment data is the different extraction and/or leaching techniques employed by various workers and which may lead to incomparable results.

Mercury concentrations in Mediterranean coastal sediments without known anthropogenic inputs range from 0.01 to 5 mg kg^{-1} on a dry weight basis (Krumgalz and Hornung, 1983). Background values derived from core samples appear to be less than 0.1

mg kg^{-1} (Baldi, present meeting). In coastal areas receiving mine effluents, concentrations up to 47 mg kg^{-1} have been reported; (Orio, present meeting). High values of mercury (5-16 mg kg^{-1}) in areas receiving effluents from chlor-alkali plants have also been reported (Orio, present meeting).

Very few data on mercury concentrations in Mediterranean sediments from the open sea exist (0.01-0.97 mg kg^{-1}) and these can be compared to concentrations in North Atlantic sediments (0.08 - 0.6 mg kg^{-1}) (Aston et al., 1972; Kosta et al., 1978).

Biomethylation of mercury in marine sediments is a well established process (see section 2.3.). However, no data exist on the rate of biomethylation of inorganic mercury in Mediterranean sediments.

4.3. Atmosphere

It is quite well established that an appreciable amount of mercury is entering the marine environment through the atmosphere. There is recent evidence (Fitzgerald et al.,1983) that the ambient concentrations of mercury in the atmosphere include contributions from the oceans, as well as other natural and anthropogenic sources.

In the Mediterranean atmosphere, Ferrara et al. (1982) have reported total mercury concentrations ranging from 2-4 ng m^{-3}. Other oceanic values range from 1-6 ng m^{-3}(Fitzgerald et al.,1983).

4.4. Marine organisms

Although a considerable amount of data has been reported on mercury concentrations in Mediterranean organisms, some discrepancies still exist for data on organisms such as plankton. This is mainly due to the fact that "plankton" consists of a large number of species of different trophic levels. In addition, the sampling techniques employed are not very specific and there may be contributions from terrigenous materials and other detritus. This feature is reflected in the results reported by different authors. Vucetic et al.(1974) reported mercury concentrations in microplankton from the Adriatic to be as high as 4.2 mg kg^{-1} (dry weight) while Kosta et al.(1978) and El-Rayis et al. (present meeting) reported values ranging from 0.050 to 0.680 mg kg^{-1} (fresh weight). The percentage of methyl mercury to total mercury in plankton has been reported to be 22% (Aboul-Dahab, present meeting).

Among molluscs, Mytilus galloprovincialis has been extensively studied and concentrations have been found to vary considerably from 0.04 to 20.4 mg kg^{-1} (fresh weight). This high variation can be attributed mainly to the capability of mussels to reflect local concentrations. Thus, mussels from relatively clean areas show considerably lower concentrations than those collected from areas receiving high inputs of mercury.

Very few data exist on the concentration of methylated mercury forms in mussels, and those that were presented during the meeting indicate that methyl mercury does not exceed 4% of the total mercury (Vukadin, present meeting).

Apart from mussels some other species of molluscs have been studied and total mercury concentrations have been reported to range between 0.02 and 0.9 mg kg^{-1} in the Mediterranean basin.

Amongst the studied Mediterranean crustacea, the ranges of mercury concentrations reported in the soft part were between 0.01 mg and 2 mg kg^{-1} on a fresh weight basis (UNEP/FAO/WHO,1983). The limited data that exist on the percentage of methyl mercury present as total mercury in crustacea indicate that it can be as high as 60% (Aboul-Dahab, present meeting).

Pelagic fish from different trophic levels have been extensively studied for their total mercury concentrations, especially in their muscle tissues. In almost all species the mercury concentrations have been reported to be higher than in the same species from other oceans (Bernhard and Renzoni, 1977).

In Boops boops an omnivorous species, the reported total mercury concentrations on a fresh weight basis vary from 0.020 to 0.432 mg kg^{-1} (UNEP/FAO/WHO,1983). The methyl mercury content represented 78 to 94% of the total mercury present in a few samples analysed (Aboul Dahab, present meeting). The most common lower trophic species in the Mediterranean is Engraulis encrasicolus which, on average, showed significally higher mercury tissue concentrations than those from Atlantic (Cumont et al., 1972; UNEP/FAO/WHO, 1983).

Considering higher trophic levels, both demersal and pelagic fish of the Mediterranean have, on average, higher total mercury concentrations than those reported from the Atlantic, Pacific and Indian Oceans (UNEP/FAO/WHO,1983).

Methyl mercury in Atlantic and Indian ocean tuna represents 59% and 40-69% of total mercury respectively (Takeda and Ueda, 1978,1978a). In the Mediterranean, methyl mercury in tuna is about 70% of the total mercury (Thibaud, present meeting).

Eggs and livers of fish-eating sea-birds were also analysed for their total mercury concentrations. In eggs obtained from the Mediterranean region, total mercury, on average, ranged from 5.4 to 6.5 mg kg^{-1} (dry weight) while those from the East Atlantic showed lower values of about 1.6 mg kg^{-1} (dry weight). In the livers of birds the mercury concentrations were higher; Mediterranean birds had on a dry weight basis 74.8 mg kg^{-1} to 86.2 mg kg^{-1} (dry weight), and the East Atlantic bird (Calonectris diomedaea) only 12.2 mg kg^{-1} (Leonzio et al., present meeting).

Extremely high mercury values have been reported in Mediterranean top predator mammals. Thibaud (present meeting), reported total mercury concentrations from the liver and spleen of dolphin Stenella coeruleoalba. In the liver, the range was 183-3620 mg kg^{-1} (dry weight), and in the spleen 11-2116 mg kg^{-1} (dry weight). In the liver and spleen 2-3% of the total mercury was found to be in the methyl form (see section 2.3.).

5. SELECTED PROCESSES IN THE MEDITERRANEAN

On the basis of existing information three main processes can be identified:

a) Sediment-sea water interactions including sedimentation and release of mercury from the sediments due to biomethylation.

b) Processes following on from (a) involving the transfer of methyl mercury through the food chain to pelagic fish such as tuna.

c) Sea water-atmosphere interactions.

Sedimentation can effectively remove (inorganic) mercury to bottom sediments. Biomethylation can release methyl mercury back into the water column and thus make it available to fish.

The following simple calculation has been undertaken using existing data from the Mediterranean as well as information on the biogeochemistry of mercury in other marine or limnic environments.

Assuming average mercury concentrations of 0.05 mg kg^{-1} and 1 mg kg^{-1} in open-ocean and coastal sediments respectively, a sedimentation and relocation rate of 1 cm 1000 $year^{-1}$ in the open-ocean and of 0.5 cm $year^{-1}$ in coastal areas, a total Mediterranean area of 2.9 X 10^6 km^2 (10% of which is coastal area) and density of sediments 2.5, the contribution of mercury to open-ocean sediments and the input and redistribution of mercury in coastal sediments were calculated to be 3.26 and 3625 t per year respectively.

If one further assumes that about 0.1 % of the mercury in sediments will be biomethylated in a year and that about 10% of this will be incorporated in Mediterranean

fish, then with a total Mediterranean fish catch of 0.86 X 10^6 t $year^{-1}$, the average methyl mercury concentration in fish can be calculated to be 0.42 mg kg^{-1}. This figure is surprisingly similar to the actual methyl mercury concentrations that have been measured in Mediterranean fish.

These rough calculations can serve to point out certain important facts:

a) The considerable difference of mercury available to coastal and open-ocean sediments can only emphasize the importance of the coastal areas of the Mediterranean in redistributing mercury and making it available to fish. Thus, the coastal zone plays the most important role in the biogeochemical cycle of mercury.

b) High mercury inputs in the coastal zone may constitute potentially serious local problems but it appears from our present knowledge that industrial inputs do not seem to influence the Mediterranean as a whole.

c) It appears that monitoring should not be aimed at establishing "average" Mediterranean mercury concentrations but rather at establishing concentrations in "hot spot" coastal areas.

The atmosphere has been recognized as an important source of mercury to the marine environment. Recent information suggests that mercury can also be volatized from the sea to the atmosphere. It is conceivable that in certain areas of relatively high productivity there would be a flux of mercury from the sea to the atmosphere, whereas in areas with high atmosphere concentrations the flux of mercury would be from the atmosphere to the sea. Simultaneous measurements of mercury in surface sea water and the atmosphere (provided reliable analyses are possible) could increase our knowledge of this important interaction.

6. CONCLUSIONS

a) A great deal of evidence has been compiled over several years which demonstrates clearly that some species such as tuna, mackerel, sardine and anchovy from the Mediterranean have mercury tissue concentrations which are higher than those found in the same species from the N. Atlantic. Also, recent data on mercury in migratory and non-migratory birds' eggs and tissues suggest that Mediterranean mercury anomalies exist.

b) Mass balance and budget calculations and models for mercury in the Mediterranean are hindered by the lack of reliable data on mercury inputs and outputs eg. river fluxes, air-sea exchanges, volcanic and geothermal contributions, industrial and sewage discharges, sedimentation rates, remobilization from sediments etc.

c) There is some evidence from studies already carried out that on a localised coastal basis, industrial discharges do result in "hot spots" and the need for site specific monitoring and assessment studies is re-affirmed. However, on an overall basis, the limitation of such discharges of mercury, eg. chlor-alkali plants, would probably not result in a measurable reduction of basin-wide mercury levels in living organisms.

d) Basic oceanographic information on the Mediterranean which is required for the interpretation of the behaviour of mercury is generally lacking.

e) Calculations making assumptions based upon data from elsewhere, in order to calculate the quantities of mercury potentially available for methylation in Mediterranean sediments, suggest that large quantities of mercury are available in coastal areas compared to

the open-ocean. The results indicate that attention to the methylation process, and its extent, should be aimed at coastal areas, especially "hot spots". The use of "average" Mediterranean data to evaluate trends in mercury contamination are ineffective.

f) Data on total mercury concentrations in Mediterranean waters are sparse, and of dubious value. Representative mercury values for sediments are also lacking.

g) Data on methyl mercury in marine biota and other components of the marine environment in the Mediterranean are also sparse, and considering that this chemical form of mercury is the one of greatest interest in terms of toxicology, there is a need to compile accurate data on methyl mercury levels in the marine environment.

7. RECOMMENDATIONS

On the basis of the above conclusions the meeting recommended:

a) that the data collected in the framework of the Mediterranean monitoring programme should not be grouped together to arrive at average values for the whole area, but should be used for trend analysis in specific areas.

b) the development of a reliable method (including sampling, storage and pretreatment) for the analysis of mercury in seawater.

c) the development and adoption of guidelines for sampling, pre-treatment, analysis and reporting of mercury concentrations in marine sediments.

d) the re-evaluation of mercury inputs and outputs in the Mediterranean.

e) the establishment of a supporting oceanographic data base which should include information pertinent to circulation and mixing processes, sedimentology, chemical interactions and biological/ecological factors.

f) the determination not only of mercury but also of methyl mercury in marine organisms in the framework of the monitoring programmes.

g) the study of the exchange of mercury at the air-sea interface subsequent to the development of a reliable method for water analysis.

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Annex I

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Annex II

LIST OF PAPERS PRESENTED

1. Aboul-Dahab O., Y. Halim and O. El-Rayis

   "Mercury species in coastal marine organisms from different trophic levels west of Alexandria".

2. Aston R. S., S. W. Fowler and N. Whitehead

   "Mercury biogeochemistry in the Mediterranean marine environment: an assessment of contamination."

3. Bacci E., F. Baldi, R. Bargagli and C.Gaggi

   "Recovery trends in a mercury polluted marine area."

4. Baldi F.

   "The biogeochemical cycle of mercury in the Tyrrhenian Sea."

5. Bernhard M.

   "A model of mercury accumulation in tuna."

6. Copin-Montégut G., P. Courai and F. Laumond

   "Occurrence of mercury in the atmosphere and waters of the Mediterranean."

7. El-Rayis O., Y. Halim and O. Aboul-Dahab

   "Total mercury in the coastal marine ecosystem west of Alexandria."

8. El-Sayed El-Nady F.

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9. Figuères G., J.M. Martin and M. Meybeck

   "A comparative study of mercury contamination in the Tagus estuary (Portugal) and major French estuaries (Gironde, Loire, Rhône)".

10. Halim Y., O. Aboul-Dahab and O. El-Rayis

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14. Najdek M., and D. Bazulic

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"Regulation and uptake of labelled iron (Fe^{55}) and labelled mercury (Hg^{203}) in the organs and flesh of Tilapia zillii Gerv, living in fresh and saline water conditions".

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18. Salihoglu I. and S. Yemenicioglu

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19. Thibaud Y.

"The role of biochemical processes in the accumulation of mercury by marine organisms".

20. Vukadin I., M. Tusek-Znidaric, A.R. Byrne and P. Stegnar

"Mercury and methyl mercury distribution in sediments and in Mytilus galloprovincialis from Kastela Bay (Central Adriatic)".

21. Zafiropoulos D.

"The biogeochemical cycle of mercury : an overview".

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